

Method for Multi-Component Recycling of Spent Lithium-Ion Battery

TECHNICAL FIELD

[0001] The present disclosure relates to a method. More specifically, the present disclosure relates to a method for multi-component recycling of spent lithium-ion battery.

BACKGROUND

[0002] The recycling of spent lithium-ion battery is a hot issue in the current society, and it is also the key to the implementation of the national strategic goal of "carbon peak and carbon neutrality". At present, the recycling process of spent lithium-ion battery faces a series of problems, the specific problems mainly include: 1) the organic binders in lithium-ion battery are difficult to remove efficiently, resulting in low recovery efficiency of electrode materials; 2) After mixing and crushing, the positive and negative electrode materials are mixed together, which is difficult to separate efficiently, reducing the efficiency of subsequent separation and purification; 3) Metals such as nickel, cobalt, manganese in the positive electrode material exist in the form of high valence, and a large amount of reducing agent or reduction pretreatment needs to be added in the leaching process, and the efficiency of preferential lithium extraction is low.

[0003] In summary, the recycle treatment of existing spent lithium-ion battery is difficult to meet the practical application needs.

SUMMARY

Technical Problems

[0004] The object of the present disclosure is to overcome the deficiencies existing in the prior art and provide a method for multi-component recycling of spent lithium-ion battery, which effectively realizes the efficient recovery of multi-component from spent lithium-ion battery, and can greatly shorten the resource process of spent lithium-ion battery. The process flow is simple, easy to operate, safe and reliable.

Technical Solutions

[0005] According to the technical solutions provided by the present disclosure, provided is a method for multi-component recycling of spent lithium-ion battery, the method for multi-component recycling comprises the following steps:

[0006] Step S1, providing at least one spent lithium-ion battery after discharge treatment, carrying out mechanical crushing and screening of the spent lithium-ion battery to obtain a fine-fraction positive and negative electrode mixture, a medium-fraction copper-aluminum current collector A and a coarse-fraction mixture of a case and a separator after mechanical crushing and screening.

[0007] Step S2, performing oxygen-free reduction roasting treatment on the fine-fraction positive and negative electrode mixture obtained above to achieve efficient reduction and magnetization of the positive electrode material.

[0008] After oxygen-free reduction roasting treatment, lithium is extracted by water leaching and filtered, and after filtration, a lithium-containing aqueous solution and leaching residue are obtained.

[0009] The obtained lithium-containing aqueous solution is concentrated and lithium is precipitated with carbonate to obtain lithium carbonate;

[0010] Carrying out magnetic separation treatment on the obtained leaching residue to obtain magnetic positive electrode material and non-magnetic mixture.

[0011] Step S3, performing froth flotation treatment on the non-magnetic mixture obtained after the magnetic separation to obtain graphite and a fine-fraction copper-aluminum current collector B;

[0012] Step S4, on the basis of a difference in density, separating and purifying the medium-fraction copper-aluminum current collector A and the fine-fraction copper-aluminum current collector B by an air table to obtain copper foil and aluminum foil respectively.

[0013] In step S1, mechanical crushing comprises shredding and impact crushing performed in sequence, wherein the means of mechanical crushing is used according to the shape and size of the crushed lithium-ion battery;

[0014] After the spent lithium-ion battery is shredded and crushed, the separator is removed by air separation, and the case material is removed by magnetoelectric separation to obtain mixed positive and negative electrode sheets, which are then subjected to secondary impact crushing.

[0015] After impact crushing, a 0.2 mm-0.25 mm sieve is used to screen to

obtain the fine-fraction positive and negative electrode mixture and the medium-fraction copper-aluminum current collector A.

[0016] In step S2, when the fine-fraction positive and negative electrode mixture is processed with oxygen-free roasting, the conditions for oxygen-free roasting are as follows: in an inert gas atmosphere, oxygen-free roasting is carried out at 700°C-750°C for 1.5-2 hours, and the inert gas atmosphere used comprises flowing nitrogen.

[0017] During oxygen-free roasting, graphite material is used as a reducing agent to reduce and magnetize the positive electrode material to obtain a magnetic separation treated material.

[0018] In step S2, when lithium is extracted by water leaching, the pH is adjusted by adding acid to convert the lithium element into a lithium salt with higher water solubility.

[0019] In the process of lithium extraction by water leaching, lithium leaching is enhanced by mechanical activation, which includes mechanical activation of ball milling.

[0020] In step S2, when the leaching residue is treated with magnetic separation, the magnetic separation treatment adopted is wet magnetic separation.

[0021] In the process of wet magnetic separation, it comprises a first magnetic separation treatment section and a second magnetic separation treatment section carried out sequentially, wherein a magnetic roller intensity of the first magnetic separation treatment section is lower than the magnetic roller intensity of the second magnetic separation treatment section.

[0022] After wet magnetic separation, the leaching solution of nickel, cobalt and manganese corresponding to the acid leaching is obtained based on a reducing agent-free acid leaching extraction process.

[0023] In step S3, during froth flotation treatment, the required collector and frother are added to the flotation slurry, wherein the amount of collector is 300 g/t - 350g/t, the amount of frother is 150g/t-200g/t, the slurry mixing time is 10 to 15 minutes, and the interval time between adding collector and frother is 5 to 10 minutes.

[0024] The added collector includes n-dodecane or kerosene.

[0025] The added frother includes methyl isobutyl carbinol or sec-octanol.

[0026] During the reducing agent-free acid leaching extraction process,

inorganic acid is used for acid leaching and no additional reducing agent is required in the acid leaching process.

[0027] In step S2, when processing the lithium-containing aqueous solution, concentration is carried out first, and then the carbonate required for lithium precipitation is added to the lithium-containing aqueous solution to obtain lithium carbonate.

Beneficial Effects

[0028] Through oxygen-free roasting heat treatment, the efficient synergy of the core links such as the removal of organic matter in the electrode materials, dissociation of electrode materials, regulation of magnetization characteristics, and reduction of transition metals is realized, greatly shortening the recycling process of spent lithium-ion battery. During oxygen-free roasting, graphite material is used as a reducing agent, achieving the reduction of high-valent transition metals in the positive electrode material and the regulation of its magnetic properties without the need for additional reductants. Magnetic separation is then used to preferentially separate and purify the magnetic positive electrode material, preventing impurity metals from entering the metallurgical process and causing difficulties in subsequent separation and purification of metal ions. The froth flotation method is used to remove metallic impurities from the graphite material, achieving purification of the negative electrode material and laying a foundation for its high-value reuse. This effectively enables the separation and recovery of all components of spent lithium-ion battery. The process is simple, easy to operate, safe, and reliable.

BRIEF DESCRIPTION OF THE DRAWINGS

[0029] FIG. 1 is a process flow diagram of the multi-component recycling method of this disclosure.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0030] The present disclosure is further described below by combining with specific figures and embodiments.

[0031] Referring to Figure 1, in order to effectively realize the efficient recycling of multiple components of spent lithium-ion battery, the multi-component recycling method for spent lithium-ion battery of the present disclosure specifically includes

the following steps:

[0032] Step S1, providing at least one spent lithium-ion battery after discharge treatment, and carrying out mechanical crushing and screening of the provided spent lithium-ion battery, so as to obtain a fine-fraction positive and negative electrode mixture, a medium-fraction copper-aluminum current collector A and a coarse-fraction mixture of a case and a separator after mechanical crushing and screening.

[0033] Specifically, for the spent lithium-ion battery, commonly used technical methods in the field are employed for discharge treatment. The specific discharge treatment methods can be selected as needed, so as to meet the requirements for discharge treatment of the spent lithium-ion battery. After discharge treatment, the spent lithium-ion battery is mechanically crushed and screened.

[0034] In the specific implementation, mechanical crushing includes shredding and impact crushing performed in sequence. The crushing time is adjusted by regulating the mesh size corresponding to the shredding and impact crushing screens to achieve the optimal crushing effect.

[0035] After the spent lithium-ion battery is shredded and crushed, the lighter separator is removed by air separation. The case material is removed by magnetoelectric separation based on different materials of the case, such as, steel cases are removed through magnetic separation, while aluminum cases are removed using electrostatic separation. This results in a mixture of positive and negative electrode sheets, and the hybrid electrode sheets are crushed by secondary impact crushing.

[0036] After impact crushing, the fine-fraction positive and negative electrode mixture and the medium-fraction copper-aluminum current collector A were obtained by sieving with a 0.2mm-0.25 mm sieve.

[0037] Specifically, the shredding stage uses a single-shaft shredding, while the impact crushing stage employs an impact crusher with a combination of cutting head and blades. During mechanical crushing, the specific working conditions of shredding and impact crushing can be selected as needed. The crushing effect is controlled by adjusting key parameters such as the size of the crusher sieve and the crushing speed. Specifically, the parameters such as the size of crusher sieve and crushing speed can be adjusted by the commonly used technical means in the technical field, which are consistent with the existing ones and can meet the actual mechanical crushing

treatment. After impact crushing and subsequent screening with a 0.2 mm–0.25 mm sieve, the fine-fraction positive and negative electrode mixture and the medium-fraction copper-aluminum current collector A can be obtained separately.

[0038] After mechanical crushing, the fine-fraction positive and negative electrode mixture, the medium-fraction copper-aluminum current collector A, as well as the coarse-fraction case and separator can be obtained through sorting. The fine-fraction positive and negative electrode mixture corresponds to the mixed black powder of positive and negative electrodes shown in Figure 1.

[0039] Step S2, performing oxygen-free reduction roasting on the fine-fraction positive and negative electrode mixture obtained above, so as to achieve efficient reduction and magnetization of the positive electrode material.

[0040] After oxygen-free reduction roasting treatment, lithium is extracted by water leaching and filtered, and after filtration, a lithium-containing aqueous solution and leaching residue are obtained.

[0041] The obtained lithium-containing aqueous solution is concentrated and lithium is precipitated with carbonate to obtain lithium carbonate.

[0042] Carrying out magnetic separation treatment of the obtained leaching residue to obtain magnetic positive electrode material and non-magnetic mixture.

[0043] In specific implementation, during the oxygen-free roasting treatment of the fine-fraction positive and negative electrode mixture, the conditions for oxygen-free roasting are as follows: the inert gas atmosphere comprises flowing nitrogen or other inert protective gases, and the oxygen-free roasting is carried out at 700°C–750°C for 1.5 to 2 hours.

[0044] During oxygen-free roasting, graphite material is used as a reducing agent to impart magnetic properties to the positive electrode material, resulting in obtaining a magnetic separation treated material.

[0045] In the embodiment of the present disclosure, in the inert gas atmosphere, the flow of inert gas can take away the pyrolysis products of organic matter, thereby avoiding affecting the reduction process. During the roasting process, high-valent transition metal reduction and lithium element conversion into water-soluble lithium salt can be achieved without adding an external reducing agent, and the positive electrode material can be efficiently magnetized.

[0046] In order to improve the efficiency of water leaching of lithium, in the

embodiment of the present disclosure, during water leaching of lithium, acid is added to adjust the pH so that the lithium element is converted into a lithium salt with higher water solubility. During the process of lithium extraction by water leaching, mechanical activation is used to enhance lithium leaching, and the mechanical activation includes ball milling mechanical activation. Specifically, the mechanical activation process uses wear-resistant and corrosion-resistant grinding balls. The optimal mechanical activation effect can be achieved by adjusting parameters such as the proportion of grinding balls of different sizes, the solid-to-liquid ratio, the grinding linear speed, and the grinding time. In practical implementation, commonly used technical methods in this field can be adopted to adjust the mechanical activation process, and the specific adjustment method can be selected based on actual needs to meet practical application requirements.

[0047] In the embodiment of the present disclosure, when processing the lithium-containing aqueous solution, the solution is first evaporated and concentrated. Then, the carbonate required for lithium precipitation is added to the lithium-containing aqueous solution to obtain lithium carbonate. Additionally, an inorganic acid such as sulfuric acid can also be added to convert the lithium carbonate into a lithium salt with higher water solubility to reduce the amount of water used.

[0048] The leaching residue is subjected to magnetic separation treatment, and the graphite, copper and aluminum in the positive electrode material can be efficiently removed by the magnetic separation method; when the leaching residue is subjected to magnetic separation treatment, the magnetic separation treatment adopted is a rotary roller wet magnetic separation. The specific conditions of the rotary roller wet magnetic separation are consistent with existing practices and can be adjusted as needed. During rotary roller magnetic separation, key parameters such as magnetic roller intensity and rotational speed are adjustable. After the wet magnetic separation, based on the reducing agent-free acid leaching-extraction process, the leaching solution of nickel, cobalt and manganese corresponding to the acid leaching is obtained.

[0049] In specific implementation, magnetic separation is used to achieve preferential recovery and purification of the magnetic positive electrode material. Before metallurgical purification, graphite and residual copper and aluminum are removed to prevent these impurity metals from entering the metallurgical process,

which could complicate the subsequent separation and purification of metal ions. The magnetic separation process uses wet magnetic separation with a combination of weak magnetic rollers and strong magnetic rollers. The first stage of magnetic separation is aimed at the problems of high material density and serious entrainment. Weak magnetic separation is used first, and strong magnetic separation is used in the second stage to achieve efficient recovery of the magnetic positive electrode material. The combination of strong magnetic separation and weak magnetic separation can select the intensity of the magnetic roller according to the slurry concentration and processing volume.

[0050] In summary, the wet magnetic separation includes a first magnetic separation treatment section and a second magnetic separation treatment section which are performed sequentially, wherein a magnetic roller intensity of the first magnetic separation treatment section is lower than the magnetic roller intensity of the second magnetic separation treatment section.

[0051] The purified powder of the positive electrode material obtained through magnetic separation is subjected to acid leaching to achieve ionization and purification of valuable metals such as nickel, cobalt, and manganese. Multi-stage extraction is then used to obtain electrode material leachates of nickel, cobalt, and manganese. Since the magnetization roasting process can simultaneously reduce high-valence metals in the magnetic electrode material, no external reducing agent is required in the acid leaching process.

[0052] In the embodiment of the present disclosure, during the reducing agent-free acid leaching extraction process, inorganic acids are used for acid leaching. Fig. 1 illustrates the case when sulfuric acid is used for acid leaching. In this embodiment, the obtained acid solutions are nickel sulfate, cobalt sulfate and manganese sulfate respectively.

[0053] Step S3, performing froth flotation treatment on the non-magnetic mixture obtained after the magnetic separation to obtain graphite and copper-aluminum current collector B.

[0054] Specifically, during the froth flotation treatment, the required collector and frother are added to the flotation slurry, wherein the amount of collector is 300 g/t - 350g/t, the amount of frother is 150g/t-200g/t, the slurry mixing time is 10 to 15 minutes, and the interval time between adding collector and frother is 5 to 10 minutes.

[0055] In the specific implementation, the added collector includes n-dodecane or kerosene. The added frother includes methyl isobutyl carbinol or sec-octanol. The added collector and frother are both analytically grade purity, which are well known to those skilled in the art and will not be described in detail here.

[0056] Step S4: on the basis of a difference in density, the medium-fraction copper-aluminum current collector A and the fine-fraction copper-aluminum current collector B are separated and purified by an air table to obtain copper foil and aluminum foil respectively.

[0057] Specifically, the air table method is used to achieve efficient separation of copper foil and aluminum foil according to their density difference, and different parameters of the air table can be used for the coarse-fraction copper foil and aluminum foil obtained by crushing and screening, as well as the fine-fraction copper foil and aluminum foil obtained by flotation, to achieve efficient separation of copper and aluminum.

[0058] In specific implementation, the air table can use existing commonly used equipment. However, for copper-aluminum current collector A and copper-aluminum current collector B of different particle sizes, key parameters such as air volume, amplitude, and feed amount are adjusted to enhance the separation efficiency of copper or aluminum current collector of varying particle sizes. The air volume, amplitude and other parameters of the air table can be set by using the commonly used technical means in the technical field. The specific parameter settings and processes can align with existing practices and should be determined based on the requirements to achieve effective separation in practical applications.

[0059] In summary, the present disclosure achieves efficient synergy in key processes such as the removal of organic matter from electrode materials, dissociation of electrode materials, regulation of magnetic properties, and reduction of transition metals through oxygen-free roasting heat treatment, which significantly shortens the resource recovery process for spent lithium-ion battery. During oxygen-free roasting, graphite material is used as a reducing agent, which means that the reduction of high-valent transition metals in the positive electrode material and the regulation of the magnetic properties of the positive electrode material can be achieved without additional reducing agent. The magnetic positive electrode material is preferentially separated and purified through magnetic separation treatment, preventing impurity

metals from entering the metallurgical process and avoiding difficulties in the subsequent separation and purification of metal ions. By using the froth flotation method to remove metal impurities from the graphite material, the purification of the negative electrode material is achieved. This lays a foundation for its subsequent high-value reutilization, effectively realizing the complete separation and recovery of all components from spent lithium-ion battery.

[0060] The foregoing description is merely a preferred embodiment of this disclosure. It should be noted that, for a person of ordinary skill in the art, various improvements and adjustments can be made without departing from the principles of the disclosure, and these improvements and adjustments should also be regarded as falling within the scope of protection of this disclosure.

CLAIMS

What is claimed is:

1. A method for multi-component recycling of spent lithium-ion battery, comprising the following steps:

Step S1, providing at least one spent lithium-ion battery after discharge treatment, carrying out mechanical crushing and screening of the spent lithium-ion battery to obtain a fine-fraction positive and negative electrode mixture, a medium-fraction copper-aluminum current collector A, and a coarse-fraction mixture of a case and a separator after mechanical crushing and screening;

Step S2, performing oxygen-free reduction roasting treatment on the fine-fraction positive and negative electrode mixture to achieve efficient reduction and magnetization of the positive electrode material;

performing water leaching of lithium and filtration after oxygen-free reduction roasting treatment, and after filtration, a lithium-containing aqueous solution and leaching residue are obtained, wherein the obtained lithium-containing aqueous solution is concentrated and lithium is precipitated with carbonate to obtain lithium carbonate; carrying out magnetic separation treatment on the obtained leaching residue to obtain magnetic positive electrode material and non-magnetic mixture;

Step S3, performing froth flotation treatment on the non-magnetic mixture obtained after the magnetic separation to obtain graphite and a fine-fraction copper-aluminum current collector B; and

Step S4, on the basis of a difference in density, separating and purifying the medium-fraction copper-aluminum current collector A and the fine-fraction copper-aluminum current collector B by an air table to obtain copper foil and aluminum foil respectively.

2. The method according to claim 1, wherein in Step S1, mechanical crushing comprises shredding and impact crushing performed in sequence, wherein the means of mechanical crushing is used according to the shape and size of the crushed lithium-ion battery;

after shredding the spent lithium-ion battery, air separation used to remove the separator, and magnetoelectric separation is used to remove the case material to obtain mixed positive and negative electrode sheets, which are then subjected to secondary impact

crushing;

after impact crushing, using a 0.2mm–0.25mm sieve to screen to obtain the fine-fraction positive and negative electrode mixture and the medium-fraction copper-aluminum current collector A.

3. The method according to claim 1, wherein in Step S2, when performing oxygen-free roasting treatment on the fine-fraction positive and negative electrode mixture, the conditions for oxygen-free roasting are as follows:

in an inert gas atmosphere, oxygen-free roasting is carried out at 700°C–750°C for 1.5 to 2 hours, wherein the inert gas atmosphere comprises flowing nitrogen;

during oxygen-free roasting, using graphite material as a reducing agent to reduce and magnetize the positive electrode material to obtain a magnetic separation treated material.

4. The method according to claim 1, wherein in Step S2, when lithium is extracted by water leaching, the pH is adjusted by adding acid to convert the lithium element into a lithium salt with higher water solubility;

in the process of lithium extraction by water leaching, lithium leaching enhanced by mechanical activation, which includes mechanical activation of ball milling.

5. The method according to claim 1, wherein in step S2, when the leaching residue is treated with magnetic separation, the magnetic separation treatment adopted is wet magnetic separation;

in the process of wet magnetic separation, comprising a first magnetic separation treatment section and a second magnetic separation treatment section carried out sequentially, wherein a magnetic roller intensity of the first magnetic separation treatment section is lower than the magnetic roller intensity of the second magnetic separation treatment section; and

after wet magnetic separation, the leaching solution of nickel, cobalt and manganese corresponding to the acid leaching is obtained based on a reducing agent-free acid leaching extraction process.

6. The method according to claim 1, wherein in step S3, during froth flotation treatment, the required collector and frother are added to the flotation slurry, wherein the amount

of collector is 300 g/t -350g/t, the amount of frother is 150g/t-200g/t, the slurry mixing time is 10 to 15 minutes, and the interval time between adding collector and frother is 5 to 10 minutes.

7. The method according to claim 6, wherein the added collector includes n-dodecane or kerosene.

8. The method according to claim 6, wherein the added frother includes methyl isobutyl carbinol or sec-octanol.

9. The method according to claim 5, wherein during the reducing agent-free acid leaching extraction process, inorganic acid is used for acid leaching and no additional reducing agent is required in the acid leaching process.

10. The method according to any one of claims 1 to 9, wherein in step S2, when processing the lithium-containing aqueous solution, concentration is carried out first, and then the carbonate required for lithium precipitation is added to the lithium-containing aqueous solution to obtain lithium carbonate.